

PATENT SPECIFICATION

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NO DRAWINGS.

Inventor :—DEREK SOUTHERN.



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COMPLETE SPECIFICATION.

A Process for the Purification of Olefines.

We, "SHELL" RESEARCH LIMITED, a British Company, of St. Helen's Court, Great St. Helen's, London, E.C.3, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

The present invention relates to a process for the purification of an olefine.

For many chemical processes a substantially pure olefine or a mixture containing substantially only olefines is advantageous, in order to obtain a good yield and rate of reaction ; and accordingly therefore, a relatively cheap, effective and rapid purification process is desirable.

According to the process of the present invention an olefine is purified by mixing it with hot silica (as hereinafter defined) to form a slurry and then removing the olefine from the slurry. It has been found that an olefine may be purified more rapidly and as efficiently by the use of this method compared with the well-known method of percolation through a column of silica gel.

The olefine which may be used in the process of the invention may be an olefine or a mixture of olefines. When the word "olefine" is used hereafter in the Specification, it includes a mixture of olefines, if desired.

Many different types of olefines or olefine mixtures may be used and the olefine may for example be a straight chain olefine for instance a straight-chain alpha olefine, or a mixture containing a large proportion of straight-chain alpha olefines. Other suitable olefines are those obtained from the Fischer-Tropsch synthesis. Olefines obtained by the dehydration of suitable alcohols or alcohol

mixtures or those obtained by the polymerisation of lower molecular weight olefines, for example propylene or butylene may also, if desired, be used.

The process of the invention is particularly applicable to those olefines obtained by the thermal or catalytic cracking of hydrocarbon feedstock, such as that produced in the refining of crude petroleum oils. Such olefines which are commonly known as cracked wax olefines are particularly preferred. Other preferred olefines are those known as cracked raffinate olefines which are obtained from the cracking of the raffinate obtained by the selective solvent extraction of heavy catalytically cracked cycle oil. The selective solvent should be a selective solvent for aromatic compounds, preferably liquid sulphur dioxide or furfural although benzene, nitrobenzene or phenol may be used. Both cracked wax and cracked raffinate olefine fractions can be fractionally distilled to obtain individual olefines, usually having not less than six and not more than eighteen carbon atoms per molecule.

Since it is preferable to carry out the process of the present invention at normal pressures this process is more applicable to the purification of olefines which are liquids at normal temperatures and pressures e.g. C₅ to C₁₅-alkenes. Higher olefines may of course be liquified by the application of heat. In order to use the lower olefines e.g. ethylene or butylene it is necessary to carry out the reaction under pressure e.g. above 45 atmospheres for propylene to ensure that the olefine is a liquid. The above described cracked-wax and cracked-raffinate olefines are particularly suitable from this point of view as they in general consist largely of

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olefines falling within the range C_6 to C_{18} which are liquid at normal temperatures and pressures.

If the olefine is an alpha olefine or a mixture of olefines containing a large proportion of alpha olefine particularly a C_6 to C_{25} olefine, and especially a cracked wax or cracked raffinate olefine, it may if desired be urea-extracted before being purified by slurring with hot silica gel. This may be very desirable when the olefine is to be polymerised, for example by the so-called Ziegler process. Urea extraction is carried out by adding the olefine to urea, preferably in aqueous or alcoholic-aqueous solution, to form a crystalline adduct, and separating and decomposing the adduct to obtain the purified olefine. A suitable method for example is described in Patent Specification 671,456 and modifications in or improvements to the method are described in Patent Specifications 671,457, 671,458, 681,246, 657,496 and 725,598 for example.

According to the process of the invention therefore the olefine (whether or not it has been urea-extracted) is mixed with hot silica to form a slurry. Although it is sometimes possible to use silica, far better results may be obtained by using silica gel, prepared for example by drying the polymer obtained from the polymerisation of colloidal silica. Accordingly silica gel and especially activated silica gel is the preferred form in which silica is used in the process of the invention. Suitable silica-gels include those marketed as "Silica-gel 90-120 mesh" (B.S.S. mesh) by the Silica Gel Co. Ltd., Davison's 923 silica gel (100-200 A.S.T.M. (U.S.) mesh) and the other Davison's silica gels i.e. 912, 922, 950, 963, 70, and 35.

In particular, it has been found that an average mesh size (B.S.S. mesh) of between about 70 and 150 for example between 90 and 120 mesh is most suitable. The SiO_2 content of the silica or silica gel should preferably be at least 98% by weight. Many of the above mentioned silica gels have a silica content of between 99.5 and 99.85, the impurities being mainly oxides of iron, sodium, calcium, titanium, zirconium and often aluminium oxide.

The silica e.g. silica gel, should have a large surface area and accordingly it has been found that a surface area of at least 500 square metres per gram is required to obtain good results. A typical suitable silica gel has been found to be one having a surface area of about 650 square metres per gram.

By the term "hot silica" or "hot silica-gel" is meant that the temperature at which the silica or silica gel is contacted with the olefine or olefine mixtures is at least $100^\circ C$. Preferably this temperature is at least $150^\circ C$, a temperature of about $200^\circ C$. or above being particularly suitable, although if desired

higher temperatures may be used. The final temperature of the slurry will of course depend on for example the quantity of silica and time of mixing, but preferably the temperature of the slurry is not allowed to fall below $30^\circ C$.

The initial temperature of the olefine or olefine mixtures with which the hot silica or silica gel is mixed need not be elevated and good results have been obtained when the olefine or olefine mixture is initially at ambient temperature, i.e. between about $10^\circ C$. and $25^\circ C$. In some cases however, the olefine or olefine mixture will have to be heated in order to liquify it.

In general good results can be obtained when using olefines which are liquid at normal temperatures by adding the hot silica or silica gel to the olefine initially at about or just above ambient temperature. Of course when the olefine and silica are mixed the temperature of the olefine will rise but unless an excessive amount of silica is used the temperature rise is usually not more than about $15^\circ C$.

The quantity of silica or silica gel required will vary according to the content of impurities in the olefine temperature and time of mixing. However, it has been found especially when purifying urea-extract olefines that less than one-third by weight of the olefine may often be used successfully, and a quantity of silica gel one-quarter that by weight of the olefine often being successful.

It is preferable for the silica to be added to the olefine all in one batch and not continuously. However, the method could be adapted to a continuous process by for example allowing silica gel to rain down on a continuously moving and agitated bed of olefine.

In carrying out the process of the invention the mixing of the olefine with the silica or silica gel to form a slurry may be achieved by agitation for example by means of stirrer or preferably a Vibro-mixer. The mixing should be carried out for at least about 10 minutes, good results being obtained if the mixing is carried out for about 30 minutes. Usually no better results are achieved by extending the time to a total of about 45 minutes.

In most cases and particularly when purifying urea-extract olefines it is not necessary to repeat this slurring technique, but, with or without separation of the olefine from the slurry, the olefine may if desired, be subjected to further slurring with silica or silica gel.

After the mixing of slurry has finished, the olefine, now substantially purified, is removed from the slurry. This may be achieved by various physical separation methods, for example distillation, fractional distillation, fractional distillation under reduced pressure, or centrifuging or filtration. Centrifuging

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or filtration of the slurry has been found to be a particularly suitable method when the olefine or olefine mixture is a liquid at normal temperatures and pressures.

- 5 The olefines especially urea-extract olefines purified by the process of the present invention are of particular use for polymerising by the Ziegler process to produce polymers which are suitable as lubricating oils for example.
- 10 Alternatively olefines purified by the process of the invention may be used for the preparation of synthetic detergents, for example alkyl benzene sulphonates.

EXAMPLE.

- 15 In this example a C_3 -cracked wax olefine cut which had been urea-extracted was purified using silica gel marketed by the Silica Gel Co. Ltd. as "90-120 mesh activated silica gel." A series of runs was carried out
- 20 using different temperatures, quantities of silica gel, and times of mixing. In each run

however, a large flask fitted with a thermometer and a Vibro-mixer having a stainless steel disc to give a downward thrust to the liquid phase was used. Olefine was added to the flask and the temperature was adjusted, if desired, before activated silica gel was added. The mixture was then agitated for ten or thirty minutes and in one run forty-five minutes after which it was filtered at the pump through a high porosity sintered-glass funnel.

The product was tested with $TiCl_4$ i.e. by adding a few drops of $TiCl_4$ to a dry sample of olefine in a dry inert atmosphere. If a precipitate was obtained (indicated that the olefine was capable of further purification), the process was repeated.

The reaction conditions and results obtained for each run were as set out below. The relationship between parts by weight and parts by volume is the same as that between the gram and the cubic centimetre.

45	Olefine (parts by volume)	Silica-gel (parts by wt.)	Temperature of olefine		Duration of mixing (minutes)	Olefine recovery % vol.	Wt. olefine to wt. of silica gel	Silica gel approximate temperature °C.
			Initial °C.	Max. °C.				
50	400	(a) 50	Ambient	34	10	90	1.3	150
		(b) 50	"	39	10	80		
		(c) 50	"	38	10	68		
	400	150	Ambient	55	10	76	1.5	150
55	400	(a) 50	96	110	10	90	2.2	150
		(b) 50	100	109	10	76		
	400	50	Ambient	34	30	88	5.1	150
	400	50	Ambient	30	45	88	5.1	150
	200	25	Ambient	35	30	83	4.8	200 to 220
	200	30	Ambient	34	30	85	4.1	200 to 220

WHAT WE CLAIM IS:—

- 60 1. A process for the purification of an olefine in which the olefine is mixed with hot silica (as hereinbefore defined) to form a slurry and the olefine is removed from the slurry.
- 65 2. A process as claimed in Claim 1, in which the olefine to be purified is a straight-chain olefine.
3. A process as claimed in any one of the preceding claims, in which the olefine is an alpha olefine.
- 70 4. A process as claimed in any one of the preceding claims, in which the olefine to be purified is a cracked-wax olefine.
5. A process as claimed in any one of

Claims 1 to 3, in which the olefine to be purified is a cracked raffinate olefine.

6. A process according to any one of the preceding claims, in which the olefine to be purified is a liquid at normal temperatures and pressures.

7. A process as claimed in any one of Claims 3 to 5, in which the olefine to be purified has previously been urea-extracted.

8. A process as claimed in any one of the preceding claims, in which silica in the form of silica-gel is used.

9. A process as claimed in Claim 8, in which the silica-gel is activated silica-gel.

10. A process as claimed in any one of the preceding claims, in which the average mesh

- size (B.S.S.) of the silica is between about 70 and 150.
11. A process as claimed in Claim 10, in which the average mesh size is between 90 and 120 mesh.
12. A process as claimed in any one of the preceding claims in which the surface area of the silica or silica gel is at least 500 sq. metres per gram.
13. A process as claimed in Claim 12 in which the surface area is about 650 sq. metres per gram.
14. A process as claimed in any one of the preceding claims in which SiO_2 content of the silica or silica gel is at least 98%.
15. A process as claimed in any one of the preceding claims in which the initial temperature of the olefine to which the silica or silica gel is added is ambient.
16. A process as claimed in any one of the preceding claims, in which the temperature of the hot silica is at least 150°C .
17. A process as claimed in Claim 16, in which the temperature is about 200°C .
18. A process as claimed in any one of the preceding claims in which the temperature of the slurry is not allowed to fall below 30°C .
19. A process as claimed in any one of the preceding claims, in which the quantity of silica used is less than one third that by weight of the olefine.
20. A process as claimed in any one of the preceding claims, in which the olefine and silica are mixed with a Vibro-mixer.
21. A process as claimed in any one of the preceding claims, in which the mixing is carried out for about 30 minutes.
22. A process as claimed in any one of Claims 6 to 20, in which the olefine is removed from the slurry by centrifuging or filtration.
23. A process as claimed in any one of the preceding claims, in which a mixture of olefines is purified.
24. A process substantially as hereinbefore described with reference to the example.
25. An olefine or a mixture of olefines whenever purified by a process as claimed in any one of the preceding claims.

DOWNES & ROBBINS,
Chartered Patent Agents,
St. Helen's Court, Great St. Helen's,
London, E.C.3,
Agents for the Applicants.

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